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COMPLETE SPECIFICATION

A Process for preparing Phthalic Acids by Oxidation of Dialkyl Benzenes

We, N. V. DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ, a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for preparing phthalic acids by oxidation of dialkyl benzenes by means of oxygen or an oxygen-containing gas, in a medium mainly consisting of an organic acid in which the dialkyl benzene is soluble, and in the presence of a catalyst and at superatmospheric pressure.

Our prior British Patent Application No. 737,439 discloses a similar process for the preparation of terephthalic acid, in which para-diisopropylbenzene is oxidized by means of oxygen or an oxygen-containing gas in a medium predominantly consisting of an organic acid, and in the presence of a catalyst comprising a manganese compound together with either a cobalt compound or a barium compound or both a cobalt compound and a barium compound. Acetic acid is preferably used as the organic acid solvent and the oxidation can be carried out at elevated pressure, e.g. an absolute pressure of 10—45 kilograms per square centimetre, preferably an absolute pressure of 20—30 kilograms per square centimetre.

After filtering off the crude phthalic acid, produced in the process of Application 737,439, a liquid remains which contains not only the organic acid solvent, starting material and intermediate products, but also undesirable volatile by-products. Before recycling this liquid to the oxidation reactor it is necessary to remove the undesirable by-products therefrom in order to prevent a build-up of such by-products in the system.

Hitherto this removal has been effected by heating the liquid and distilling off the vola-

tile by-products. It has now been found, however, that when this liquid, which contains the by-products and starting material dissolved therein, is heated in the absence of oxygen, undesirable side reactions occur, as a result of which, after recycling the heated liquid, the phthalic acid yield is adversely affected.

Difficulties can also occur as a result of cooling the reactor, which is required by the exothermic reaction, in that solid oxidation product can become deposited on the walls or internal cooling elements.

An object of the present invention is to provide an improved process for the production of phthalic acids by the oxidation of dialkyl benzenes.

According to the present invention a process for preparing a phthalic acid comprises oxidising a dialkyl benzene by means of oxygen or an oxygen-containing gas present in sufficient excess adequately to remove volatile by-products and acetic acid, in a medium consisting mainly of acetic acid, in the presence of a catalyst comprising a manganese compound together with either a cobalt compound or a barium compound or both a cobalt compound and a barium compound and under a pressure between 2 and 10 atmospheres (absolute), the reaction conditions being such that volatile by-products and acetic acid are removed from the reaction mixture in the vapour phase and substantially all the heat of reaction is withdrawn from the reaction mixture by the evaporation of said volatile by-products and acetic acid therefrom.

It has been found that when the oxidation is carried out under these conditions the said volatile by-products disappear to a sufficient extent to allow the reaction liquid, after removal of the phthalic acid, to be recycled without it being necessary to remove further undesirable components under non-oxidative conditions. If the oxidation is carried out at a higher pressure than 10 atmospheres less

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5 favourable results are obtained and it has been proved that it is not possible to remove these by-products satisfactorily. In carrying out the process of the present invention the pressure is preferably between 4 and 8 atmospheres (absolute).

The said volatile by-products are particularly formic acid, water, formaldehyde and methyl acetate.

10 The process of the present invention is not restricted to the oxidation of para-di-isopropyl benzene.

15 In carrying out the present invention the metals, whose compounds form the catalyst system, may occur in different valency states. Preferably the metal compound is a salt: salts of aliphatic carboxylic acids comprising from 1 to 8 (inclusive) carbon atoms per molecule are particularly preferred.

20 By carrying out the oxidation in such a way that the reaction heat is substantially completely (i.e. approximately 90% or more) removed from the reaction mixture by evaporation of acetic acid and volatile by-products, large reaction vessels without any cooling elements may be used, since the remaining 10% of the reaction heat is readily lost by radiation and through the other heat losses which usually occur in chemical plant.

30 Preferably in the process of the present invention the oxidation is carried out at a temperature between 100°C. and 140°C. At these temperatures the decomposition of acetic acid, which begins to occur to a considerable extent

at 150°C., is only very slight.

Favourable results are obtained in the process of the present invention by operating with an excess of oxygen of at least 100 mol.% of that required to react with the dialkyl benzene to form the corresponding phthalic acid.

The variables, temperature, pressure and the rate at which the oxygen or oxygen-containing gas is introduced cannot, of course, be independently chosen. A constant reaction rate is usually aimed at, at which as much heat is generated as is removed by the gas stream and radiation, so that the temperature remains constant. The gas flow rate is preferably kept as constant as possible, the temperature being regulated by adjusting the pressure within the limits which are required according to the invention. If desired, the pressure can be kept constant and the temperature regulated by adjusting the gas flow rate.

The oxygen-containing gas may be air or another gas mixture, preferably having a higher oxygen content than air. Pure or practically pure oxygen may also be used, if desired.

The table below shows the amounts of air theoretically required for the oxidation of di-isopropyl benzene, the removal of the by-products, and for removing all the reaction heat by evaporation, i.e. assuming no heat loss through the wall of the reaction vessel. The feed rates are shown for different pressures at a constant reaction temperature of 140°C.

Pressure atm. abs.	Mols of air per mol. of oxidized di-isopropyl benzene
4	85
6	150
8	210
10	270

70 In the process of the present invention acetic acid is withdrawn in vapour form simultaneously with the volatile by-products and in order to recover this acid, the gas mixture withdrawn from the reactor may be condensed, and the liquid thus obtained distilled in the presence of an azeotroping agent, (preferably benzene). It is possible in this way to obtain acetic acid which is sufficiently pure to be recycled to the reactor. The gas stream may also be introduced directly into the distillation column for the azeotropic distillation, together with the azeotroping agent, without first being condensed. The latter variant is more advantageous from the point of view of heat economy. When the acetic acid recovered, e.g. 85 in the above-mentioned ways, eventually be-

gins to contain too much methyl acetate, it is advisable to draw off and remove a bleed of acid either periodically or continuously.

The process of the present invention can be carried out in a reaction vessel comprising an autoclave fitted with stirring means or alternatively in a tube-shaped reaction vessel in which mixing is effected by the ascending gas bubbles.

The effect of the reaction temperature on the course of the reaction is illustrated by the results of three oxidation runs carried out in a 5-litre, stainless steel autoclave provided with a stirrer, para-di-isopropyl benzene being the substance oxidized. The results are shown in the following Table:—

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Run	Reaction temperature (°C.)	Terephthalic acid yield (mol. % calculated on hydrocarbon converted)	Equivalent weight of the terephthalic acid (determined by acidimetric titration)
I	165	71	83.8
II	150	75	84.4
III	125	82	84.8

The process of the present invention is illustrated by the following Example in which the parts are by weight unless otherwise stated and the relationship between parts by weight and parts by volume is that between the gram and the litre:—

EXAMPLE.

Air was passed through an acetic acid solution consisting of 250 parts of para-di-isopropyl benzene, 640 parts of para-isopropyl benzoic acid, 7.7 parts of cobalt acetate, 7.7 parts of manganese acetate and 2,300 parts of 98% acetic acid in a tube-shaped reaction vessel with an internal diameter of 6.4 centimetres and a length of 180 centimetres at 140° C. and 6.5 atmospheres (absolute). The average flow rate of the air was approximately 700 parts by volume per hour. During the oxidation process which lasted for 10 hours, acetic acid was continuously pumped in (total 8823 parts) while in addition 100 parts of para-di-isopropyl benzene were added to the

reaction mixture every hour (i.e. total 900 parts). Acetic acid and a number of light products were removed from the reaction vessel in the stream of unconsumed oxidation air, and on cooling yielded a total of 9720 parts of condensate and 6640 parts by volume of unconsumed gas (measured at room temperature and atmospheric pressure).

Upon completion of the oxidation the contents of the reaction vessel were filtered, yielding 2396 parts of filtrate and 1021 parts of a wet terephthalic acid cake which was washed with acetone and then dried at 140° C. The amount of acetone filtrate was 1000 parts. The dried terephthalic acid amounted to 692 parts (viz. a yield of 74 mol.% calculated on di-isopropyl benzene) and the equivalent weight determined by acidimetric titration was 83.8.

An analysis of the condensate obtained from the gas stream removed gave the following results:

acetic acid	-	-	-	89.61%	by weight
formic acid	-	-	-	3.04%	" "
formaldehyde	-	-	-	0.32%	" "
methyl acetate	-	-	-	0.31%	" "
para-di-isopropyl benzene	-	-	-	1.60%	" "
para-isopropyl acetophenone	-	-	-	0.02%	" "
para-isopropyl benzoic acid	-	-	-	0.28%	" "
water	-	-	-	4.34%	" "
neutral products	-	-	-	0.04%	" "
					<u>99.56% by weight</u>

The following figures were obtained on an analysis of the first filtrate obtained from the reaction mixture:

acetic acid	-	-	-	69.50%	by weight
formic acid	-	-	-	0.77%	" "
formaldehyde	-	-	-	0.09%	" "
methyl acetate	-	-	-	0.11%	" "
para-di-isopropyl benzene	-	-	-	2.01%	" "
para-isopropyl acetophenone	-	-	-	0.90%	" "
para-isopropyl benzoic acid	-	-	-	21.24%	" "
water	-	-	-	1.04%	" "
					<u>95.66% by weight</u>

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The acetone filtrate contained 9.18% by weight of para-isopropyl benzoic acid, 1.2% by weight of para-di-isopropyl benzene, and 21.8% by weight of acetic acid.

- 5 The oxygen, carbon monoxide, and carbon dioxide content of the gas removed was continuously measured, while, moreover, after approximately $2\frac{1}{2}$, 5, $7\frac{1}{2}$ and 10 hours gas samples were taken, the saturated hydrocarbon content of which was also determined. These analyses showed that a total of 1280 parts of oxygen had been consumed that a total of 111 parts of carbon monoxide, 375 parts of carbon dioxide and 17 parts of saturated hydrocarbons (average composition C_2H_6) had been withdrawn from the reaction vessel.

What we claim is:—

1. A process for preparing a phthalic acid, which comprises oxidising a dialkylbenzene by means of oxygen or an oxygen-containing gas present in sufficient excess adequately to remove volatile by-products and acetic acid, in a medium consisting mainly of acetic acid, in the presence of a catalyst comprising a manganese compound together with either a cobalt compound or a barium compound or both a cobalt compound and a barium compound and under a pressure between 2 and 10 atmospheres (absolute), the reaction conditions being such that volatile by-products and acetic acid are removed from the reaction mixture in the vapour phase and substantially all the heat of reaction is withdrawn from the

reaction mixture by the evaporation of said volatile by-products and acetic acid therefrom. 35

2. A process as claimed in claim 1, wherein an excess of oxygen of at least 100 mol % over that required to react with the dialkyl benzene to form the corresponding phthalic acid, is used. 40

3. A process as claimed in claim 1 or claim 2, wherein the reaction is carried out at a temperature between 100° C. and 140° C.

4. A process as claimed in any one of the preceding claims, wherein the oxidation is carried out under a pressure between 4 and 8 atmospheres (absolute). 45

5. A process as claimed in any one of the preceding claims, wherein the catalyst comprises in combination a cobalt salt and a manganese salt. 50

6. A process as claimed in any one of the preceding claims, wherein the dialkyl benzene is a di-isopropyl benzene.

7. A process as claimed in claim 6, wherein para-di-isopropyl benzene is oxidised. 55

8. A process for preparing a phthalic acid substantially as hereinbefore described with reference to the Example.

9. A phthalic acid when prepared by the process claimed in any one of the preceding claims. 60

H. I. DOWNES,
Agent for the Applicants,
St. Helen's Court, Great St. Helen's,
London, E.C.3.

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